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FR-A- 2 537 150

CHEMICAL ABSTRACTS, vol. 108, no. 14, 4th
April 1988, page 91, abstract no. 114204y,
Columbus, Ohio, US; & JP-A-62 250 066
(CANON K.K.) 30-10-1987

CHEMICAL ABSTRACTS, vol. 103, no. 18, 14th
November 1985, page 70, abstract no.
143353y, Columbus, Ohio, US; & JP-A-60 081
249 (MITSUBISHI CHEM. IND. K.K.) 09-05-1985

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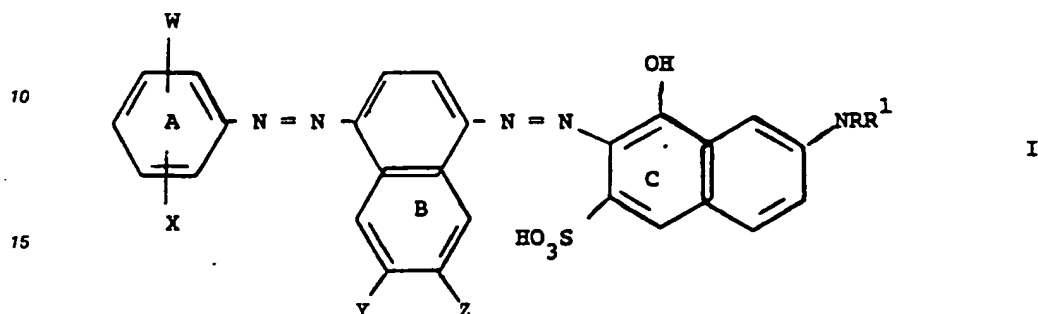
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CHEMICAL ABSTRACTS, v 1. 95, no. 6, 10th
August 1981, page 75, abstract n . 44707b,
Columbus, Ohio, US; I.D. LEVCHENKOVA et
al.: "Disazo dyes from alkylaminosalicylic
acids" & LATV. PSR ZINAT. AKAD. VESTIS,
KIM. SER. 1981, (2), 234-8

Description

This specification describes an invention relating to an anionic dye and particularly a black anionic dye which has differential water-solubility dependent upon pH.

According to the present invention there is provided a dye which, in the free acid form, has the formula:



wherein

W is COOH

X is H, COOH, SO₃H, halo, hydroxy, nitro, cyano, C₁₋₆-alkyl, C₁₋₆-alkoxy, or C₁₋₆-acylamino;

Y is H, COOH or SO₃H;

Z is H, COOH or SO₃H;

R & R¹ are each independently H or C₁₋₆-alkyl substituted by 0, 1 or 2 -COOR² groups;

R² is H or C₁₋₆-alkyl;

provided that there are at least two COOH groups and that the number of COOH groups is equal to or greater than the number of SO₃H groups.

X is preferably selected from SO₃H, chloro, bromo, hydroxy, nitro, cyano, C₁₋₄-alkyl especially methyl, C₁₋₄-alkoxy especially methoxy, C₁₋₄-alkylcarbonylamino, especially acetamido and, more especially, from H and COOH.

It is preferred that R² is H, methyl or ethyl.

It is especially preferred that X is H or COOH; R¹ is H; and R is H, CH₂COOH or CH₂CH₂COOH.

It is preferred that the dye of Formula I contains from 2 to 4 COOH groups. It is also preferred that at least one, and more especially at least two, COOH groups are attached directly to aromatic carbon atoms.

Where X is H, the COOH group on Ring A may be in the ortho, meta or para position with respect to the azo group but is preferably in the meta or para position. However, it is preferred that X is COOH and that the two COOH groups are in the 3,5-, 3,4- or 2,5- positions on Ring A.

It is preferred that there are not more than two SO₃H groups, i.e. that only one of X, Y and Z is SO₃H. It is also preferred that there are the same number of COOH and SO₃H groups or an excess of 1 or 2 COOH groups.

Examples of diazo components from which Ring A may be derived are

2-aminobenzoic acid	3-amino-6-chlorobenzoic acid
3-aminobenzoic acid	2-amino-4-chlorobenzoic acid
4-aminobenzoic acid	2-amino-5-chlorobenzoic acid
2-aminophthalic acid	3-amino-4-chlorobenzoic acid
3-aminophthalic acid	2-chloro-3-aminobenzoic acid
4-aminoisophthalic acid	2-chloro-4-aminobenzoic acid
5-aminoisophthalic acid	2-amino-5-bromobenzoic acid
2-aminoisophthalic acid	3-amino-4-fluorobenzoic acid
2-aminoterephthalic acid	2-amino-5-methylbenzoic acid
2-amino-6-methylbenzoic acid	3-amino-2-methylbenzoic acid
3-methyl-4-aminobenzoic acid	3-hydroxy-4-aminobenzoic acid
3-amino-4-methylbenzoic acid	3-amino-5-hydroxybenzoic acid
3-amino-4-methoxybenzoic acid	3-amino-4-hydroxybenzoic acid
3-methoxy-4-aminobenzoic acid	2-hydroxy-3-aminobenzoic acid
2-n-butoxy-4-aminobenzoic acid	2-amino-4-nitrobenzoic acid
2-amino-5-sulphobenzoic acid	3-nitro-4-aminobenzoic acid
2-amino-4-sulphobenzoic acid	3-amino-5-nitrobenzoic acid
2-amino-6-hydroxybenzoic acid	2-nitro-3-aminobenzoic acid
2-hydroxy-5-aminobenzoic acid	2-nitro-5-aminobenzoic acid
2-amino-5-hydroxybenzoic acid	3-acetylamino-5-aminobenzoic acid

Examples of suitable couplers from which the central group B is derived are:

1,6-Cleves acid	8-amino-2-naphthoic acid
1,7-Cleves acid	5-amino-2-naphthoic acid
Mixed Cleves acids	5-amino-2,3-dicarboxynaphthalene

Examples of suitable couplers from which the third group C is derived are:

Gamma acid	N-butyl-Gamma acid
N-methyl-Gamma acid	N-carboxymethyl-Gamma acid
N,N-dimethyl-Gamma acid	N,N-di(carboxymethyl)-Gamma acid
N,N-diethyl-Gamma acid	N-(beta-carboxyethyl)-Gamma acid

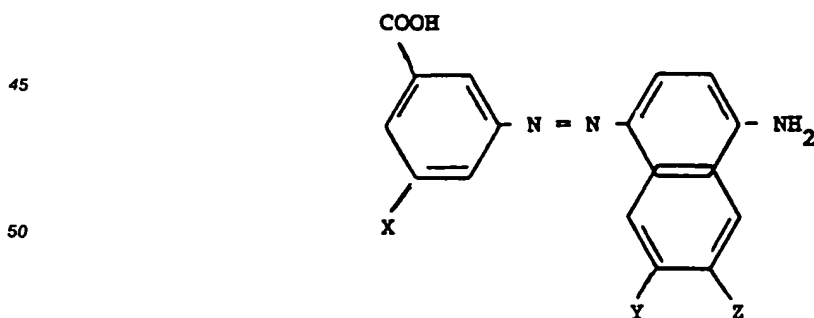
Examples of suitable compounds of Formula I are given in the following table:

	X	W	Y	Z	R	R'
	3-COOH	5-COOH	H	H	H	H
	3-COOH	5-COOH	COOH	H	H	H
5	3-COOH	5-COOH	H	COOH	H	H
	3-COOH	5-COOH	H	SO ₃ H	H	H
	3-COOH	5-COOH	SO ₃ H	H	H	H
	3-COOH	5-COOH	COOH	COOH	H	H
	H	4-COOH	H	COOH	H	H
10	3-COOH	4-COOH	H	H	CH ₂ COOH	CH ₃
	2-COOH	5-COOH	H	SO ₃ H	CH ₂ COOH	H
	3-COOH	5-COOH	SO ₃ H	H	CH ₂ COOH	H
	3-COOH	5-COOH	H	H	C ₂ H ₄ COOH	H
	3-COOH	5-COOH	H	COOH	CH ₂ COOH	H
15	3-COOH	5-COOH	H	SO ₃ H	CH ₂ COOH	H
	3-COOH	5-COOH	H	SO ₃ H	C ₂ H ₄ COOH	H
	3-COOH	5-COOH	H	H	CH ₂ COOH	H
	H	3-COOH	COOH	H	H	H
	H	3-COOH	H	COOH	H	H
20	H	2-COOH	H	H	H	H
	H	4-COOH	H	COOH	CH ₂ COOH	CH ₂ COOH
	2-COOH	5-COOH	H	H	CH ₃	CH ₃
	2-COOH	3-COOH	H	H	C ₂ H ₅	C ₂ H ₅
	2-COOH	4-COOH	H	SO ₃ H	H	H
25	3-COOH	4-COOH	H	H	H	C ₄ H ₉
	3-CH ₃	5-COOH	H	SO ₃ H	H	H
	2-CH ₃	5-COOH	H	SO ₃ H	H	H
	3-Cl	6-COOH	H	SO ₃ H	H	H
	2-OCH ₃	5-COOH	H	SO ₃ H	H	H
30	3-SO ₃ H	6-COOH	H	SO ₃ H	H	H
	4-SO ₃ H	6-COOH	H	SO ₃ H	H	H

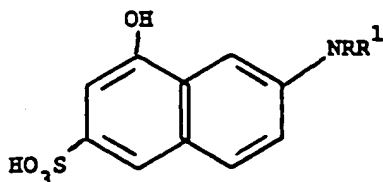
In the form of salts with a base, especially an alkali metal, ammonia or substituted ammonia and mixtures thereof, at pH 7.5 and above, especially from pH 7.5 to 9.0, dyes of Formula I are very soluble in water, generally to the extent of 10% or more by weight. However, the water-solubility drops sharply below pH 7.5 and below pH 6 they are virtually insoluble in water and aqueous media.

The present dye can be converted into its salt with ammonia or an amine by dissolving the dye in the form or a salt with an alkali metal, acidifying with a mineral acid, adjusting the solution to pH 9-9.5 with ammonia or the amine and removing alkali metal chloride ions by dialysis.

The present dyes can be made by diazotising a compound which in the free acid form is of the formula:



and coupling with a substituted naphthalene of the formula:



It has been found that a dye of Formula I can be dissolved in an aqueous medium above pH 7.5, preferably from pH 7.5 to pH 9, at normal concentrations which, depending on type of ink required can be up to 20% by weight, but is preferably from 5 to 15% by weight, so that it can be applied, by any suitable technique, especially ink-jet printing, to a paper substrate. After application of the ink to the substrate and evaporation of the solvent, the dye is at a pH determined by the surface of the paper substrate. The natural pH of many paper substrates is such that the dye will be in an environment from pH 5 to 7. Because the water-solubility of the dye is much lower below pH 7 and virtually zero at pH 6, it will be more resistant to removal from the substrate by washing, i.e. it will have a high water-fastness.

We have found also that the water-fastness of the dyes on the paper is increased if they are printed from an aqueous medium in the form of an ammonium or substituted ammonium salt. Examples of amines used to form such salts include methylamine, dimethylamine, trimethylamine, ethylamine, n-propylamine, iso-propylamine, n-butylamine, iso-butylamine, sec-butylamine, tert-butylamine, piperidine, pyridine, morpholine, allylamine, diethylamine, triethylamine and mixtures thereof. It is not essential that the dyes are completely in the form of the ammonium salt or substituted ammonium salt and mixed alkali metal and either ammonium salt or substituted ammonium salt are effective, especially those in which at least 50% of the cations are ammonium or substituted ammonium ions.

If the natural pH value of the paper surface is significantly above pH 6, this can be adjusted downwards, by the addition to the ink of a salt of an acid with a volatile base, such as ammonia. When the ink dries the base evaporates to leave the free acid which will lower the pH of the paper surface in the region of the dye. To minimise damage to the paper it is preferred to use a weak acid, such as acetic acid.

A suitable ink comprises a solution of one or two dyes according to Formula I in an aqueous medium.

The ink preferably contains from 0.5% to 20%, more preferably from 0.5% to 15%, and especially from 1% to 10%, by weight of the dye based on the total weight of the ink.

Liquid media used for preparing the present ink include water and mixtures of water with various water-soluble organic solvents. The water-soluble organic solvents include C₁-C₄ alkanols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, isobutanol; amides such as dimethylformamide and dimethylacetamide; ketones or ketone alcohols such as acetone and diacetone alcohol; ethers such as tetrahydrofuran and dioxane; polyalkylene glycols such as polyethylene glycol and polypropylene glycol; alkylene glycols and thioglycols containing C₂-C₆ alkylene groups such as ethylene glycol, propylene glycol, butylene glycol, triethylene glycol; thiodiglycol, hexylene glycol, and diethylene glycol; other polyols such as glycerol, 1,2,6-hexanetriol; and lower alkyl ethers of polyhydric alcohols such as 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, 2-[2-(2-methoxyethoxy)-ethoxy]ethanol and 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol.

Preferred water-soluble organic solvents among these are glycols and glycol ethers, such as ethylene glycol, diethylene glycol, triethylene glycol and 2-methoxy-2-ethoxy-2-ethoxyethanol; and polyethylene glycols with molecular weights up to 500. A preferred specific solvent mixtures is a binary mixture of water and diethylene glycol.

A suitable process for the application of an ink as hereinbefore defined to a paper substrate comprises forming the ink into small droplets by ejection from a reservoir through a small orifice by the application of heat so that the droplets of ink are directed at the paper substrate.

This printing process is conventionally referred to as thermal ink jet printing and is used to form a record on the paper substrate by the programmed application of pulses of heat to the ink adjacent to the orifice during relative movement between the paper substrate and the reservoir.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise indicated.

Example 1Stage 15 1-amino-4-(3,5-dicarboxyphenylazo)-7-sulphonaphthalene

5-Aminoisophthalic acid (18.1g, 0.1M) was stirred in water (150ml) at room temperature and 2N NaOH added to form a solution at pH 8.0. 2N NaNO₂ solution (50ml) was added and the mixture stirred to homogenise. The solution was added gradually to a mixture of ice/water (150ml) and 36% HCl (50ml) at 10 5 °C and the resulting suspension stirred for ½ hour at 50 °C. Sulphamic acid solution (10%) was added in order to remove excess nitrous acid.

1,7-Cleaves acid (22.3g, 0.1M) was dissolved in water (150ml) and 32% NaOH solution at pH 8.5. Na₂CO₃ (10g) was added and the solution cooled to 10 °C. To this solution was added the above diazo suspension at pH 8.0 to pH 9.0 by the addition of Na₂CO₃ solution (20%). The orange solution was stirred 15 for 1 hour at 10 °C.

10% NaCl (w/v) was added followed by 36% HCl to pH 5.0. The precipitated dye was collected by filtration and washed with NaCl solution (10%, 200ml).

Stage 2

20 The paste from Stage 1 (0.1M) was dissolved in water (100ml) and 2N NaOH solution at pH 9.0. 2N NaNO₂ solution (50ml) was added and the mixture stirred 3 minutes. The solution was added gradually to a mixture of ice/water (150ml) and 36% HCl (50ml) at 5 °C using rapid agitation. The resulting suspension was stirred 1h at 5 °C. Sulphamic acid solution (10%) was added in order to remove excess nitrous acid.

25 Gamma acid (23.9g, 0.1M) was dissolved in water (150ml) and 2N NaOH solution at pH 9.0. Na₂CO₃ - (10g) was added and the solution cooled to 10 °C. To this was added the above diazo suspension, while holding the pH at 8.0 to pH 9.0 with 20% Na₂CO₃ solution. The solution was stirred for 1 hour at 10 °C and the pH adjusted to 5.5 by the addition of glacial acetic acid.

30 The precipitated dye was collected by filtration and washed with dilute acetic acid solution (5%). The paste was redissolved in water (150ml) and 2N NaOH solution at pH 9.0. The solution was heated to 50 °C and NaCl (15% w/v) added and the precipitated dye collected by filtration and washed with 10% NaCl solution (100ml). The product was the tetrasodium salt of 1-hydroxy-2-(4-[3,5-dicarboxy-phenylazo]-7-sulpho-naphth-1-ylazo)-3-sulpho-7-aminonaphthalene.

35 Example 2Stage 140 1-Amino-4-(3,5-dicarboxyphenylazo)naphthalene

5-Aminoisophthalic (18.1g, 0.1M) was diazotised by the method of Example 1.

1-Naphthylamine (14.3g, 0.1M) was dissolved in water (300ml) and 36% HCl (15ml) at 70 °C and cooled to room temperature. The resulting suspension was added to the above diazo suspension at 10 °C and the pH adjusted to 4.5 by the addition of sodium acetate. The mixture was stirred for 18 hours and the dye 45 collected by filtration and washed with water (100ml).

Stage 2

50 The paste from Stage 1 (0.1M) was then reacted with Gamma acid by the method of Example 1, Stage 2. The product was the trisodium salt of 1-hydroxy-2-(4-[3,5-dicarboxyphenylazo]-naphth-1-ylazo)-3-sulpho-7-aminonaphthalene.

Examples of specific inks are:

Ink	Dye No. (parts)	Liquid medium and other components (parts)
1	1 (2.5)	Water (60) Ethylene glycol (40)
2	2 (2.5)	as Ink 1
3	1 (4.0)	Water (85) Diethylene glycol (15)
4	2 (4.0)	as Ink 3
5	1 (5.0)	Water (90) Diethylene glycol (10)
6	2 (5.0)	as Ink 5
7	1 (5.0)	Water (65) Glycerol (25) Triethanolamine (10)
8	2 (3.0)	as Ink 7
9	1 (3.5)	Water (80) Ethylene glycol (15) Polyethylene glycol (MW 200)(5)
10	2 (3.5)	as Ink 9

When each of these inks was printed onto plain paper using a piezo or thermal ink-jet printing machine, the printed image obtained had high resistance to water.

Example 3

The dye obtained as in Example 1 was stirred in water (400ml) at pH 8-9 until a complete solution was obtained. The solution was then slowly added to a mixture of concentrated hydrochloric acid (45ml) and water (50ml) and the suspension stirred for 30 minutes and then filtered.

The paste was stirred in water (300ml) and conc.ammonium hydroxide added to raise the pH to 9-9.5. The solution was then dialysed to remove chloride ions and then evaporated to give the mixed ammonium sodium salt of 1-hydroxy-2-(4-[3,5-dicarboxyphenylazo]-7-sulphonaphth-1-ylazo)-3-sulpho-7-aminonaphthalene.

Inks were prepared as in Example 2 and when printed onto plain paper using a thermal ink jet printing machine, the printed image obtained had very high resistance to water. When the paper carrying the printed image was immersed in water or sprayed with a jet of water there is virtually no colour loss or deterioration of print quality.

Example 4

(a) In place of the ammonium hydroxide used in Example 3 there were used separately methylamine, dimethylamine and trimethylamine to give the respective mixed amine-sodium salts of 1-hydroxy-2-(4-[3,5-dicarboxyphenylazo]-7-sulphonaphth-1-ylazo)-3-sulpho-7-aminonaphthalene.

Inks were prepared as in Example 2 and when printed onto plain paper using a thermal ink jet printing machine, the printed image obtained had a very high resistance to water.

(b) In place of ammonium hydroxide used in Example 3 there may be used ethylamine, n-propylamine, iso-propylamine, n-butylamine, iso-butylamine, sec-butylamine, tert-butylamine, piperidine, pyridine, morpholine, allylamine, diethylamine, triethylamine.

Exempl 5

The dye prepared as in Example 2 was converted to the mixed ammonium-sodium salt by the method of Example 3.

When converted to an ink and printed onto plain paper using a thermal ink-jet printing machine the printed image obtained has very high resistance to water.

Example 6

5 In place of the 18.1g of 5-aminoisophthalic acid used in Example 2 there is used 18.1g of 4-aminophthalic acid. The product 1-hydroxy-2-(4-[3,4-dicarboxyphenylazo]naphth-1-ylazo)-3-sulpho-7-aminonaphthalene was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet printing machine, the printed image
10 has a very high resistance to water.

Example 7

15 In place of the 22.3g of 1,7-Cleves acid used in Example 1 there is used 22.3g of 1,6-Cleves acid. The product 1-hydroxy-2-(4-[3,5-dicarboxyphenylazo]-6-sulphonaphth-1-ylazo)-3-sulpho-7-aminonaphthalene was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet printing machine the printed image showed very high resistance to water.

Example 8

20 In place of the 22.3g of 1,7-Cleves acid used in Example 1 there is used 18.7g of an approximately 50/50 mixture of 5-amino-2-naphthoic acid and 8-amino-2-naphthoic acid. The product consisted of a mixture of 1-hydroxy-2-(4-[3,5-dicarboxyphenylazo]-6-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene and 1-hydroxy-2-(4-[3,5-dicarboxyphenylazo]-7-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene. It was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet printing machine the printed image showed very high resistance to water.

Example 9

30 In place of the 23.9g of Gamma-acid used in Example 1 there is used 29.7g of N-carboxymethyl-Gamma acid. The product 1-hydroxy-2-(4-[3,5-dicarboxyphenylazo]-6-sulphonaphth-1-ylazo)-3-sulpho-7-carboxymethylaminonaphthalene was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet machine the printed image showed high resistance to water.

Example 10

40 In place of the 23.9g of Gamma-acid used in Example 1 there is used 31.1g of N-beta-carboxyethyl-Gamma acid. The product 1-hydroxy-2-(4-[3,5-dicarboxyphenylazo]-6-sulphonaphth-1-ylazo)-3-sulpho-7-beta-carboxyethylaminonaphthalene was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet machine, the printed image showed high resistance to water.

Example 11

45 In place of the 23.9g of Gamma-acid used in Example 2 there is used 29.7g of N-carboxymethyl-Gamma acid. The product 1-hydroxy-2-(4-[3,5-dicarboxyphenylazo]-naphth-1-ylazo)-3-sulpho-7-carboxymethylaminonaphthalene was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet machine the printed image showed high resistance to water.

Example 12

55 In place of the 23.9g of Gamma-acid used in Example 2 there is used 31.1g of N-beta-carboxyethyl-Gamma acid. The product 1-hydroxy-2-(4-[3,5-dicarboxyphenylazo]-naphth-1-ylazo)-3-sulpho-7-beta-carboxyethylaminonaphthalene was converted to the mixed ammonium-sodium salt by the method of Example 3.

When made into an ink and printed onto plain paper using a thermal ink jet machine the printed image showed high resistance to water.

Example 13

In place of the 18.1g of 5-aminoisophthalic acid used in Example 8 there is used 13.7g of p-aminobenzoic acid. The product consists of a mixture of 1-hydroxy-2-(4-[4-carboxyphenylazo]-6-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene and 1-hydroxy-2-(4-[4-carboxyphenylazo]-7-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene.

It was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet machine the printed image showed high resistance to water.

Example 14

In place of the 13.7g of p-aminobenzoic acid used in Example 13 there is used 13.7g of m-aminobenzoic acid. The product consists of a mixture of 1-hydroxy-2-(4-[3-carboxyphenylazo]-6-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene and 1-hydroxy-2-(4-[3-carboxyphenylazo]-7-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene. When converted to the mixed ammonium-sodium salt by the method of Example 3 and made into an ink and printed onto plain paper using a thermal ink jet machine the printed image showed high resistance to water.

Example 15

In place of the 13.7g of p-aminobenzoic acid used in Example 13 there is used 13.7g of anthranilic acid. The product consists of a mixture of 1-hydroxy-2-(4-[2-carboxyphenylazo]-6-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene and 1-hydroxy-2-(4-[2-carboxyphenylazo]-7-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene. It was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet machine the printed image showed high resistance to water.

Example 16

In place of the 18.1g of 5-aminoisophthalic acid used in Example 2 there is used 18.1g of aminoterephthalic acid. The product 1-hydroxy-2-(4-[2,5-dicarboxyphenylazo]naphth-1-ylazo)-3-sulpho-7-aminonaphthalene was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet printing machine the printed image had a high resistance to water.

Example 17

In place of the 18.1g of 5-aminoisophthalic acid used in Example 2 there is used 18.1g of 3-aminophthalic acid. The product 1-hydroxy-2-(4-[2,3-dicarboxyphenylazo]naphth-1-ylazo)-3-sulpho-7-aminonaphthalene was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet printing machine the printed image had a high resistance to water.

Example 18

In place of the 22.3g of 1,7-Cleaves acid used in Example 1 there is used 23.1g of 5-amino-2,3-dicarboxynaphthalene. The product 1-hydroxy-2-(4-[3,5-dicarboxyphenylazo]-6,7-dicarboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet printing machine the printed image showed high resistance to water.

Example 19

In place of the 18.1g of 5-aminoisophthalic acid used in Example 1 there is used 18.1g of 4-aminoisophthalic acid. The product 1-hydroxy-2-(4-[2,4-dicarboxyphenylazo]-7-sulpho-naphth-1-ylazo)-3-sulpho-7-aminonaphthalene was converted to the mixed ammonium-sodium salt by the method of Example 3.

Example 20

In place of the 18.1g of 5-aminoisophthalic acid used in Example 2 there is used 18.1g of 4-aminoisophthalic acid. The product 1-hydroxy-2-(4-[2,4-dicarboxyphenylazo]-naphth-1-ylazo)-3-sulpho-7-aminonaphthalene was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet printing machine the printed image showed very high resistance to water.

Example 21

The dye obtained as in Example 1 was stirred in water (400ml) at pH 8-9 until a complete solution was obtained. The solution was acidified with concentrated hydrochloric acid until the pH falls below 3. The precipitate was filtered off, added to water (400ml) and concentrated ammonium hydroxide added until the pH was 7.5-8.0. The solution was then acidified with concentrated hydrochloric acid and the precipitated dye filtered off. After repeating the ammonia addition and reprecipitation with acid three times and finally dissolving in water by adding ammonium hydroxide to pH 8, the solution was dialysed to remove chloride ions and then evaporated. The product was virtually 100% ammonium salt of 1-hydroxy-2-(4-[3,5-dicarboxyphenylazo]-7-sulphonaphth-1-ylazo)-3-sulpho-7-aminonaphthalene.

When converted to an ink and printed onto plain paper using a thermal ink-jet printing machine, the printed image obtained has very high resistance to water. When the paper carrying the printed image was immersed in water or sprayed with a jet of water there is virtually no colour loss or deterioration of print quality.

Alternatively, the ammonium salt of the dye of Example 1 can be obtained by passing a solution of the sodium salt of the dye down a column containing the ammonium form of a cation exchange resin.

Example 22

In place of the 18.1g of 5-aminoisophthalic acid used in Example 8 there is used 15.1g of 2-amino-5-methylbenzoic acid. The product consisted of a mixture of 1-hydroxy-2-(4-[2-carboxy-4-methyl-phenylazo]-6-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene and 1-hydroxy-2-(4-[2-carboxy-4-methylphenylazo]-7-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene. It was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet printing machine the printed image showed very high resistance to water.

Example 23

In place of the 18.1g of 5-aminoisophthalic acid used in Example 8 there is used 15.1g of 3-amino-4-methylbenzoic acid. The product consisted of a mixture of 1-hydroxy-2-(4-[2-methyl-5-carboxyphenylazo]-6-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene and 1-hydroxy-2-(4-[2-methyl-5-carboxyphenylazo]-7-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene. It was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet printing machine the printed image showed very high resistance to water.

Example 24

In place of the 18.1g of 5-aminoisophthalic acid used in Example 8 there is used 17.1g of 2-amino-4-chlorobenzoic acid. The product consisted of a mixture of 1-hydroxy-2-(4-[2-carboxy-5-chlorophenylazo]-6-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene and 1-hydroxy-2-(4-[2-carboxy-5-chlorophenylazo]-7-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene. It was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet printing machine the printed image showed very high resistance to water.

Example 25

In place of the 18.1g of 5-aminoisophthalic acid used in Example 8 there is used 16.7g of 2-amino-4-methoxybenzoic acid. The product consisted of a mixture of 1-hydroxy-2-(4-[2-methoxy-5-carboxyphenylazo]-6-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene and 1-hydroxy-2-(4-[2-methoxy-5-carboxyphenylazo]-7-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene. It was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet printing machine the printed image showed very high resistance to water.

Example 26

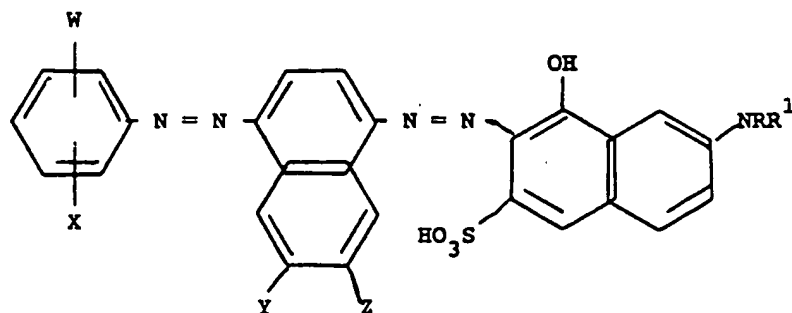
In place of the 18.1g of 5-aminoisophthalic acid used in Example 8 there is used 21.7g of 2-amino-4-sulphobenzoic acid. The product consisted of a mixture of 1-hydroxy-2-(4-[2-carboxy-5-sulphophenylazo]-6-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene and 1-hydroxy-2-(4-[2-carboxy-5-sulphophenylazo]-7-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene. It was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet printing machine the printed image showed high resistance to water.

Example 27

In place of the 18.1g of 5-aminoisophthalic acid used in Example 8 there is used 21.7g of 2-amino-5-sulphobenzoic acid. The product consisted of a mixture of 1-hydroxy-2-(4-[2-carboxy-4-sulphophenylazo]-6-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene and 1-hydroxy-2-(4-[2-carboxy-4-sulphophenylazo]-7-carboxynaphth-1-ylazo)-3-sulpho-7-aminonaphthalene. It was converted to the mixed ammonium-sodium salt by the method of Example 3. When made into an ink and printed onto plain paper using a thermal ink jet printing machine the printed image showed high resistance to water.

Claims

1. A dye which, in the free acid form, has the formula



wherein

W is COOH

X is selected from H, COOH, SO₃H, halo, hydroxy, nitro, cyano, C₁₋₆-alkyl, C₁₋₆-alkoxy and C₁₋₆-acylamino;

Y is H, COOH or SO₃H;

Z is H, COOH or SO₃H;

R & R¹ are each independently H or C₁₋₆-alkyl substituted by 0, 1 or 2 -COOR² groups; and

R² is H or C₁₋₆-alkyl;

provided that there are at least two COOH groups and that the number of COOH groups is equal to or greater than the number of SO₃H groups.

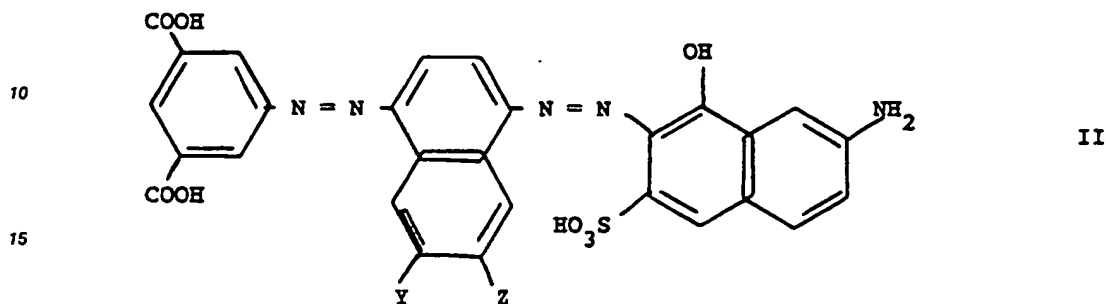
2. A dye according to claim 1 in which X is H or COOH.

3. A dye according to claim 1 or 2 in which R¹ is H and R is H, CH₂COOH or C₂H₄COOH.

4. A dye according to any one of Claims 1 to 3 containing 2, 3 or 4 CO₂H groups attached directly to an aromatic carbon atom.

5. A dye which, in its free acid form, has the formula

5



20 wherein

Y is H or SO₃H

Z is H, COOH or SO₃H.

25 6. A composition of dyes comprising the dye according to Claim 5 in which Y is SO₃H and Z is H and the dye according to Claim 5 in which Y is H and Z is SO₃H.

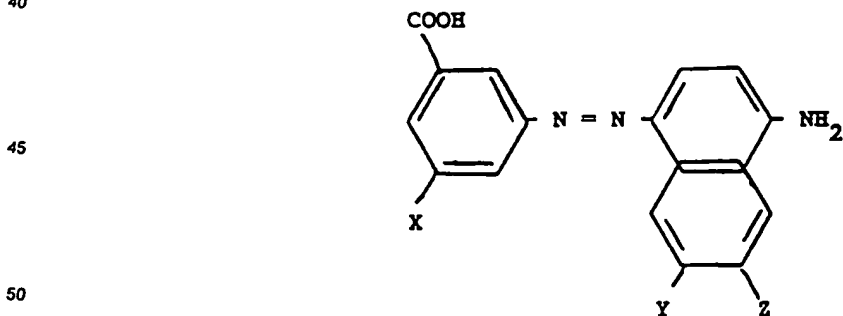
7. A composition of dyes comprising the dye according to Claim 5 in which Y is H and Z is COOH and the dye according to Claim 5 in which Y is COOH and Z is H.

30 8. A dye according to any of claims 1 to 7 in the form of its salt with at least one of the basic compounds selected from the alkali earth metals, ammonia, methylamine, dimethylamine, trimethylamine, ethylamine, n-propylamine, iso-propylamine, n-butylamine, iso-butylamine, sec-butylamine, tert-butylamine, piperidine, pyridine, morpholine, alkylamine, diethylamine and triethylamine.

35 9. A dye according to Claim 8 in the form of its sodium, ammonium, or mixed sodium/ammonium salt.

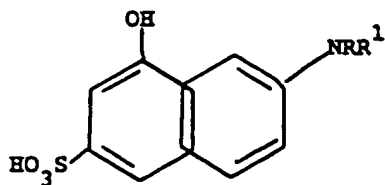
10. A process for the manufacture of dyes as claimed in any one of Claims 1 to 7 which comprises diazotising a compound which in the free acid form is of the formula:

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and coupling with a substituted naphthalene of the formula:

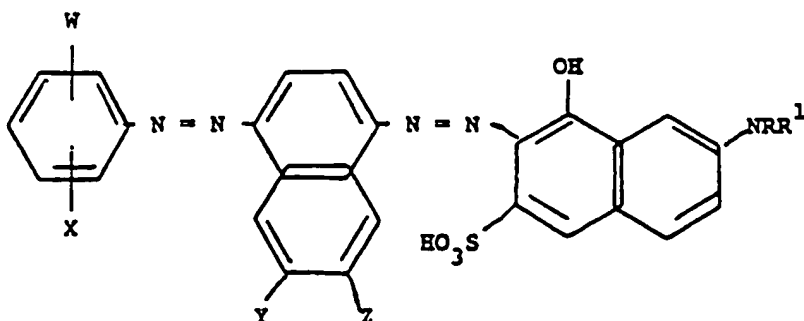
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11. A process for the preparation of a dye according to any one of Claims 1 to 9 in the form of its salt with ammonia or an amine which comprises dissolving the dye in the form or a salt with an alkali metal, acidifying with a mineral acid, adjusting the solution to pH 9-9.5 with ammonia or the amine and removing alkali metal chloride ions by dialysis.
12. An ink comprising a dye or a composition of dyes according to any one of Claims 1 to 9 or a salt thereof dissolved in an aqueous medium.
13. An ink comprising a solution in an aqueous medium of one or two dyes according to any one of Claims 1 to 9
14. An ink according to Claim 12 wherein the dye is as claimed in Claim 5 in which only one of Y and Z is SO₃H.
15. An ink according to Claim 13 wherein in one of the dyes Y and Z are both H.
16. An ink according to Claim 13 wherein in one of the dyes Y is H and Z is SO₃H.
17. An ink according to any one of Claims 12 to 16 wherein the aqueous medium is water or a mixture of water and a water-soluble organic solvent.
18. An ink according to any one of Claims 12 to 17 wherein the amount of the dye is up to 20% by weight.
19. An ink according to any one of Claims 12 to 18 wherein the pH of the aqueous medium is from 7.5 to 9.

Patentansprüche

1. Farbstoff, welcher in Form der freien Säure die Formel



I

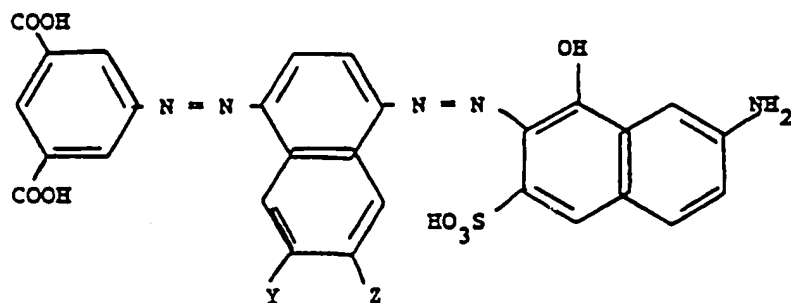
besitzt, worin

W für COOH steht;
X ausgewählt ist aus H, COOH, SO₃H, Halogeno, Hydroxy, Nitro, Cyano, C₁₋₆-Alkyl, C₁₋₆-Alkoxy und C₁₋₆-Acylamino;

- Y für H, COOH oder SO₃H steht;
 Z für H, COOH oder SO₃H steht;
 R und R¹ jeweils unabhängig für H oder C₁₋₆-Alkyl, das durch 0, 1 oder 2 Gruppen -COOR² substituiert ist, stehen; und
 5 R² für H oder C₁₋₆-Alkyl steht;

mit der Maßgabe, daß mindestens 2 Gruppen COOH vorliegen und daß die Anzahl der Gruppen COOH genau so groß ist wie oder größer ist als die Anzahl der Gruppen SO₃H.

2. Farbstoff nach Anspruch 1, bei welchem X für H oder COOH steht.
- 10 3. Farbstoff nach Anspruch 1 oder 2, bei welchem R¹ für H und R für H, CH₂COOH oder C₂H₄COOH steht.
4. Farbstoff nach einem der Ansprüche 1 bis 3, welcher 2, 3 oder 4 Gruppen CO₂H enthält, die direkt an ein aromatisches Kohlenstoffatomen gebunden sind.
- 15 5. Farbstoff, welcher in Form der freien Säure die Formel

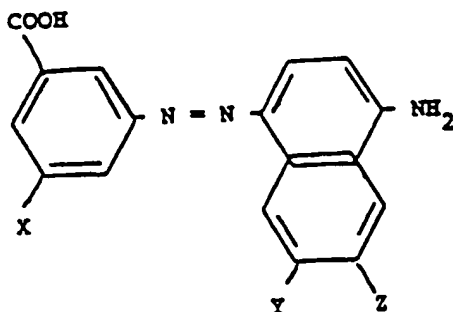


II

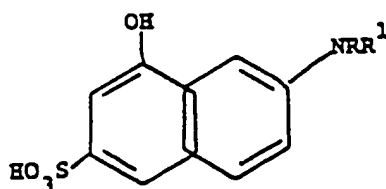
besitzt, worin

- Y für H oder SO₃H steht; und
 Z für H, COOH oder SO₃H steht.

- 35 6. Farbstoffzusammensetzung, welche einen Farbstoff nach Anspruch 5, bei welchem Y für SO₃H und Z für H steht, und einen Farbstoff nach Anspruch 5, bei welchem Y für H und Z für SO₃H steht, enthält.
7. Farbstoffzusammensetzung, welche einen Farbstoff nach Anspruch 5, bei welchem Y für H und Z für COOH steht, und einen Farbstoff nach Anspruch 5, bei welchem Y für COOH und Z für H steht, enthält.
- 40 8. Farbstoff nach einem der Ansprüche 1 bis 7 in Form eines Salzes mit mindestens einer basischen Verbindung, die ausgewählt ist aus den Erdalkalimetallen, Ammoniak, Methylamin, Dimethylamin, Trimethylamin, Ethylamin, n-Propylamin, Isopropylamin, n-Butylamin, Isobutylamin, sec-Butylamin, tert-Butylamin, Piperidin, Pyridin, Morpholin, Alkylaminen, Diethylamin und Triethylamin.
- 45 9. Farbstoff nach Anspruch 8, in Form seines Natrium-, Ammonium- oder gemischten Natrium-/Ammonium-Salzes
- 50 10. Verfahren zur Herstellung eines Farbstoffs nach einem der Ansprüche 1 bis 7, bei welchem eine Verbindung, die in Form der freien Säure die Formel



aufweist, diazotiert und mit einem substituierten Naphthalin der Formel

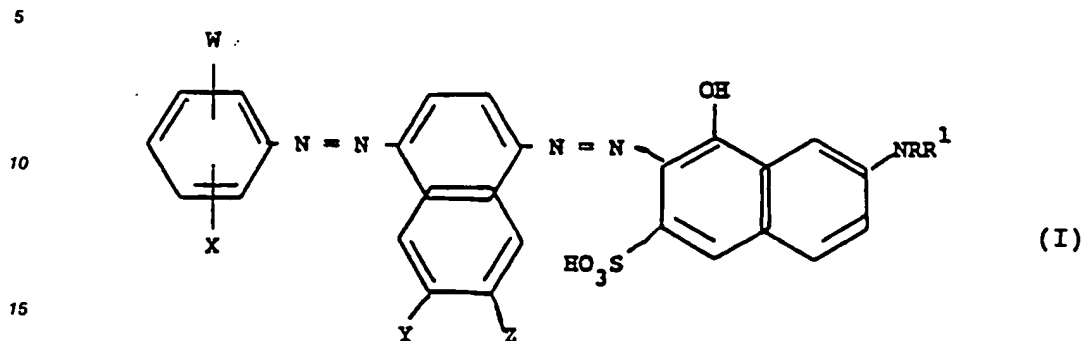


gekuppelt wird.

11. Verfahren zur Herstellung eines Farbstoffs nach einem der Ansprüche 1 bis 9 in Form eines Salzes mit Ammoniak oder einem Amin, bei welchem der Farbstoff in Form eines Salzes mit einem Alkalimetall aufgelöst wird, die Lösung mit einer Mineralsäure angesäuert wird, die Lösung mit Ammoniak oder dem Amin auf einen pH von 9 bis 9,5 eingestellt wird und Alkalimetallchloridionen durch Dialyse entfernt werden.
12. Tinte, welche einen Farbstoff oder eine Farbstoffzusammensetzung nach einem der Ansprüche 1 bis 9 oder ein Salz davon als Lösung in einem wäßrigen Medium enthält.
13. Tinte, welche aus einer Lösung eines oder zweier Farbstoffe nach einem der Ansprüche 1 bis 9 in einem wäßrigen Medium besteht.
14. Tinte nach Anspruch 12, bei welcher der Farbstoff die in Anspruch 5 genannte Form aufweist, wobei nur eines der Symbole Y und Z für SO₃H steht,
15. Tinte nach Anspruch 13, bei welcher in einem der Farbstoffe Y und Z beide für H stehen.
16. Tinte nach Anspruch 13, bei welcher in einem der Farbstoffe Y für H und Z für SO₃H steht.
17. Tinte nach einem der Ansprüche 12 bis 16, bei welcher das wäßrige Medium Wasser oder ein Gemisch aus Wasser und einem wasserlöslichen organischen Medium ist.
18. Tinte nach einem der Ansprüche 12 bis 17, bei welcher die Menge des Farbstoffs bis zu 20 Gew.% beträgt.
19. Tinte nach einem der Ansprüche 12 bis 18, bei welcher der pH des wäßrigen Mediums 7,5 bis 9 beträgt.

Revendications

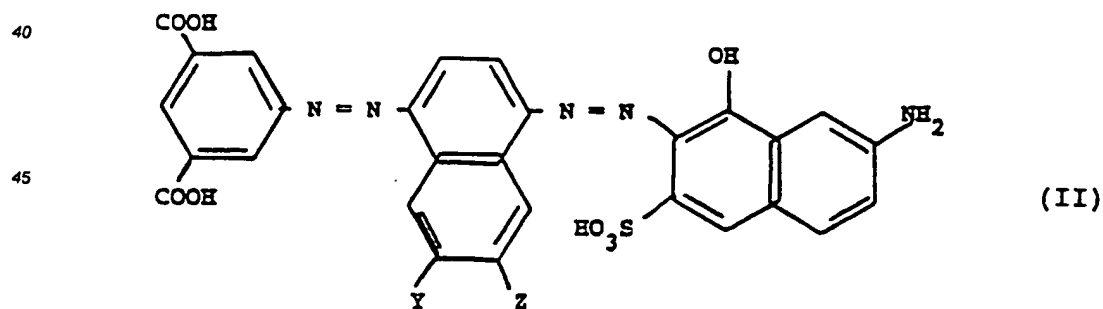
1. Colorant qui, dans sa forme acide libre, a la formule :



dans laquelle :

- 20 W est COOH;
 X est choisi parmi H, COOH, SO₃H, halo, hydroxy, nitro, cyano, alcoyle en C₁₋₆, alcoxy en C₁₋₆ ou acylamino en C₁₋₆;
 Y est H, COOH ou SO₃H;
 Z est H, COOH ou SO₃H;
 25 R & R¹ sont chacun indépendamment H ou alcoyle en C₁₋₆ substitué par 0, 1 ou 2 radicaux COOR², et
 R² est H ou alcoyle en C₁₋₆; pourvu qu'il y ait au moins deux radicaux COOH et que le nombre de radicaux COOH soit égal ou supérieur au nombre de radicaux SO₃H.

- 30 2. Colorant suivant la revendication 1, dans lequel X est H ou COOH.
 3. Colorant suivant la revendication 1 ou 2, dans lequel R¹ est H et R est H, CH₂COOH ou C₂H₄COOH.
 4. Colorant suivant l'une quelconque des revendications 1 à 3, contenant 2, 3 ou 4 radicaux CO₂H
 35 attachés directement à un atome de carbone aromatique.
 5. Colorant qui, dans sa forme acide libre, a la formule :

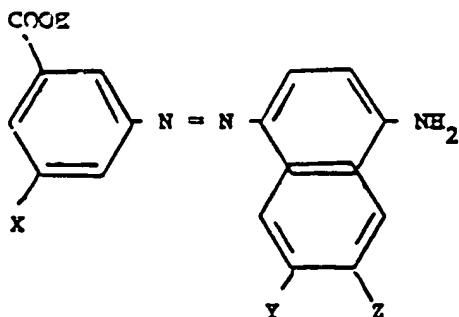


où

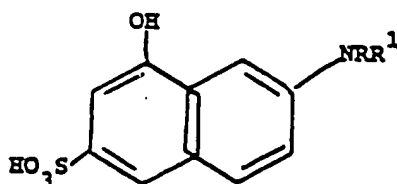
- Y est H ou SO₃H;
 Z est H, COOH ou SO₃H.

- 55 6. Composition de colorants comprenant le colorant suivant la revendication 5, dans lequel Y est SO₃H et Z est H et le colorant suivant la revendication 5 dans lequel Y est H et Z est SO₃H.

7. Composition de colorants comprenant le colorant suivant la revendication 5, dans lequel Y est H et Z est COOH et le colorant suivant la revendication 5 dans lequel Y est COOH et Z est H.
8. Colorant suivant l'une quelconque des revendications 1 à 7, sous la forme de son sel avec au moins un des composés basiques choisis parmi les métaux des terres alcalines, l'ammoniaque, la méthylamine, la diméthylamine, la triméthylamine, l'éthylamine, la n-propylamine, l'isopropylamine, la n-butylamine, l'isobutylamine, la s-butylamine, la t-butylamine, la pipéridine, la pyridine, la morpholine, une alcoylamine, la diéthylamine et la triéthylamine.
9. Colorant suivant la revendication 8, sous la forme de son sel de sodium, d'ammonium ou de sodium-ammonium mixte.
10. Procédé de fabrication de colorants suivant l'une quelconque des revendications 1 à 7, qui comprend la réaction de diazotation d'un composé qui, sous sa forme acide libre a la formule :



et couplage avec un naphthalène substitué de la formule :



11. Procédé pour la préparation d'un colorant suivant l'une quelconque des revendications 1 à 9, sous la forme de son sel avec l'ammoniaque ou une amine, qui comprend la dissolution du colorant sous la forme d'un sel avec un métal alcalin, acidification avec un acide minéral, ajustage de la solution à pH 9-9,5 avec de l'ammoniaque ou l'amine et élimination des ions chlorure du métal alcalin par dialyse.
12. Encre comprenant un colorant ou une composition de colorants suivant l'une quelconque des revendications 1 à 9, ou un sel de ceux-ci dissous dans un milieu aqueux.
13. Encre comprenant une solution dans un milieu aqueux d'un ou de deux colorants suivant l'une quelconque des revendications 1 à 9.
14. Encre suivant la revendication 12, où le colorant est suivant la revendication 5, dans lequel seulement un des Y et Z est SO₃H.
15. Encre suivant la revendication 13, où, dans un des colorants, Y et Z sont tous deux H.

16. Encre suivant la revendication 13, où, dans un des colorants, Y est H et Z est SO_3H .

17. Encre suivant l'une quelconque des revendications 12 à 16, où le milieu aqueux est de l'eau ou un mélange d'eau et d'un milieu organique soluble dans l'eau.

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18. Encre suivant l'une quelconque des revendications 12 à 17, où la quantité de colorant est jusqu'à 20% en poids.

19. Encre suivant l'une quelconque des revendications 12 à 18, où le pH du milieu aqueux est de 7,5 à 9.

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